Rocky Mountain Conference on Magnetic Resonance

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Article 1

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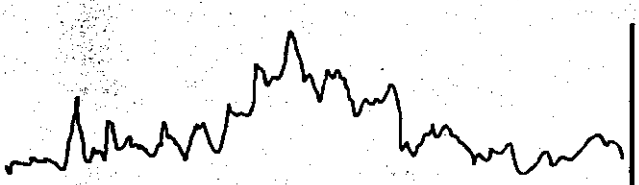
18th Annual Rocky Mountain Spectroscopy Conference



18TH ANNUAL ROCKY MOUNTAIN SPECTROSCOPY CONFERENCE

FINAL PROGRAM — ABSTRACTS

AUGUST 2–3, 1976

UNIVERSITY OF DENVER CAMPUS

DENVER, COLORADO

Sponsored by the

ROCKY MOUNTAIN SECTION

of the

SOCIETY FOR APPLIED SPECTROSCOPY

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GENERAL INFORMATION

Sponsor

The Rocky Mountain Section of the Society for Applied Spectroscopy invites spectroscopists and friends of spectroscopy to join us in Denver for the 18th Annual Rocky Mountain Spectroscopy Conference. The format of the conference favors, as in previous years, friendly exchange in an informal atmosphere. The technical program promises to be an excellent one, covering topical subjects from a broad spectrum of applied spectroscopy. Some of the latest in instrumentation, laboratory equipment, and analytical aids will be exhibited during the conference. An opportunity for a relaxing and enjoyable social evening will be provided for the conferees and their guests attending the conference banquet.

Registration

Conference registration will be in the main lobby of the University of Denver Business Administration Building. No pre-registration is required. The registration desk will be open throughout the conference, starting at 7:45 a.m. on Monday, Aug. 2. Coffee, pastry, and orange juice will be available from 7:45—10:00 a.m. on Aug. 2. Please make checks payable to the Rocky Mountain Section, Society for Applied Spectroscopy (RMS-SAS). Registration badges will be necessary for admission to all technical program sessions. Registration fees are as follows:

All conferees (except full-time students) — $15.00
Students (full-time) — — — — — — — — — — $ 4.00
Banquet — — — — — — — — — — — — — — $ 6.00

Abstracts of technical papers are published on the conference final program, which is available at registration.

Location

Please note that the conference has moved this year from one of the downtown Denver hotels to the campus of the University of Denver. The conference technical program will be presented in

the Lindsay Auditorium, and adjoining lobby areas of the College of Business Administration Building, University of Denver. The address is 2020 South Race Street. Arrangements have been made for free parking for the conference, at lots located just south of the Business Administration Building, and across the street on the southwest corner of Asbury and Race Streets. The conference will arrange for private transportation from area hotels (South Denver) to the campus facilities, for those requesting this service.

Accommodations

Conferees from outside the immediate Denver area must arrange housing facilities for their stay in Denver. The conference committee has arranged for a block of rooms to be held for conferees, through July 25, 1976, at the Writers' Manor Hotel, and also for rooms to be made available through the Centennial Conference Center at the University Campus. Reservation addresses for these facilities and others in the area of the campus are:

Writers' Manor Hotel: 1730 S. Colorado Blvd.
Denver, CO 80222

Holiday Inn Hotel: 1475 South Colorado Blvd.
Denver, CO 80222

Centennial
Conference Center: University of Denver
Centennial Conference Center
Denver, CO 80210
Phone: 303/753-2721

Visitor Information

Information on the Denver area may be obtained from the Denver Convention and Visitors Bureau, 225 West Colfax Avenue, Denver, CO 80202 (Phone: 303/982-1505). Information on events commemorating the Centennial anniversary of statehood for Colorado may be obtained by contacting the Colorado Centennial/Bicentennial Commission, 901 Sherman St., Denver CO 80200 (Phone: 303/837-1876). Available brochures will be exhibited at the registration desk during the conference.

Social Evening

The convention banquet will be served at 7:30 p.m., Aug. 2, on the patio area of the historic Phipps House Mansion at the Lawrence C. Phipps Memorial Conference Center. Breast of Chicken and Baron of Beef will highlight the buffet dinner, prepared by the University of Denver Staff, which enjoys an excellent reputation for its cuisine. Tickets for the banquet will be available at the registration desk until noon, Monday.

The banquet will be preceded by a hosted cocktail hour (admission by banquet ticket) from 6:00 to 7:30 p.m. Small groups will be given guided tours of the Phipps Mansion during the cocktail hour. The tour is presented by members of the University of Denver Women's Auxiliary, and includes a history of the house and the family of Senator Phipps.

An illustrated presentation, entitled "Look Up and See", will be given by Ms. Lyn Spenst, Historic Denver, Inc., following the banquet. The presentation will be on the history of Denver and early architecture used in some of the more noteworthy mansions, and what is being done to preserve Denver's past.

In the spirit of the Bicentennial, special recognition will be given charter members of the Rocky Mountain Section, for their efforts in organizing the local SAS chapter 19 years ago.

Exhibits

Current state-of-the art instruments and equipment will be on display in the lobby area outside the auditorium. Exhibitors arranged for thus far include:

KEVEX Corporation
The Buhrke Company
Siemens Corporation
Ortec, Incorporated
R. H. Allen Scientific Glass Company
INCOS, Incorporated
TRACOR, Incorporated

Dri X-Ray Conference

The 25th Annual Applications of X-Ray Analysis Conference will be conducted at the same location on August 4, 5, and 6. For additional information, contact C. O. Rudd, Metallurgy and Materials Science Division, Denver Research Institute, University of Denver, Denver, Colorado 80210 (Phone: 303/753-2141).

Inquiries

For additional information on the RMS-SAS Conference, contact Keith J. Grossaint, Rockwell International, Rocky Flats Plant, P. O. Box 464, Golden, Colorado 80401 (Phone: 303/497-2153).

CONFERENCE SCHEDULE

Registration: 7:45 a.m. to 3:00 p.m. daily
Exhibits: 8:30 a.m. to 4:00 p.m. daily

Monday, August 2, 1976

Welcome: 8:55 a.m. (Robert Heidel, Chairman, Rocky Mountain Section-Society for Applied Spectroscopy)

Technical Program—

Session (I)

"Spectroscopy Applied to Fossil Fuels," Chairman: Dr. J. H. Weber, ERDA, Laramie Energy Research Center, Laramie, Wyoming.

9:00 Keynote Address—Behind the Scenes in Fossil Fuels/Applied Spectroscopy

Dr. Andrew Decora, Director, Energy Research and Development Administration, Laramie Energy Research Center, Laramie, Wyoming.

Dr. Andrew Decora has been director of the Laramie Energy Research Center since December, 1974. In this position, he has the responsibility for managing energy research in the fields of insitu recovery of oil shale, tar sands, and coal gasification.

Prior to assuming his present position, Dr. Decora served as assistant to the Assistant Director of Exploration and Extraction, for the U.S. Department of Interior. Dr. Decora's duties were in the area of Oil Shale Research and Development,

Planning and Programming. His recent contributions have been through participation in the preparation of the Department's Prototype Oil Shale Leasing Program, for which he received a commendation from Interior Secretary Morton, and through participation in the Federal Energy Administrations Project Independence study on oil shale.

Dr. Decora's previous work at the Laramie Energy Research Center was in basic research related to the spectroscopy and the kinetics and mechanisms of shale oil components. His research work involved the thermal-photochemical-and oxidation-reactions of shale oil compounds. His research extended to the fields of infrared, ultraviolet, nuclear magnetic resonance, and mass spectrometry. He is the author or co-author of twenty publications in the above research areas.

9:30 Identification of the Organic Components Isolated from Waste Water Produced During an In Situ Retorting of Tar Sands

F. A. Barbour and F. D. Guffey, ERDA, Laramie Energy Research Center, Laramie, Wyoming.

The development of tar sands as a usable energy source will in many cases require the use of in situ processes which will generate polluted water as well as the desired oil. Convenient methods of handling these pollutants must be developed concurrently with the technology of the recovery process. The identification of the components in the waste water is necessary to aid in the development of a clean up process. The water samples discussed in this paper were produced during an in situ reverse burn of a tar sand deposit near Vernal, Utah. The organic portion was removed from the water by liquid-liquid extraction using ether as the solvent. Gas chromatography was used as a means of separating the extracted organic portion. Infrared spectroscopy on the trapped fractions, as well as combined gas chromatography-mass spectroscopy were used to identify the major organic components in the waste water.

9:50 Combined Gas Chromatography-Mass Spectroscopic Identification of Phenolic

Components Isolated from Coal Tars Collected from an Underground Coal Gassification Experiment

F. D. Guffey and S. B. King, ERDA, Laramie Energy Research Center, Laramie, Wyoming.

The identification of products obtained from processes used to recover energy from alternate fossil fuel sources is of practical importance. Knowledge of the recovery products provides additional data for the evaluation of the process and may indicate other environmental and economic considerations for the utilization of the energy source.

Coal tars collected from an underground coal gasification experiment have been separated into acid, base and neutral fractions. Combined gas chromatography-mass spectroscopy has been used to study the acid fractions. The mass spectroscopic results and the column retention of the components were used to identify phenol and many of the alkyl substituted phenolic isomers in the acid fractions.

10:10 Characterization of Saturate Hydrocarbon Fractions from Fossil Fuel Sources by Mass Spectroscopy

R. A. Heppner and F. D. Guffey, ERDA, Laramie Energy Research Center, Laramie, Wyoming.

The development and utilization of alternate energy sources dictates the need for characterization of fossil fuel energy sources and the products that are obtained by different recovery processes. The application of existing spectroscopic methods and techniques for the characterization of the products obtained from new energy recovery processes is one of the missions of our laboratory. We have successfully characterized saturated hydrocarbon fractions from alternate energy sources with the use of both high and low resolution mass spectroscopy. Mass spectroscopic techniques can be used to obtain information about (1) the presence of any components containing heteroatoms, (2) the possible overlap of hydrocarbon z series, (3) the carbon number spread for compound types present in the sample, and (4) an estimated compositional analysis of the compound types present in the sample. The results obtained from the study of

the oil saturate fraction from a synthetic oil obtained from coal will be presented.

10:30 Carbon-13 Chemical Shifts of Saturated Heterocycles of Groups IV, V, and VI

D. A. Netzel, ERDA, Laramie Energy Research Center, Laramie, Wyoming.

The carbon-13 chemical shifts were measured for six-membered saturated heterocycles from groups IV, V, and VI. It has been found that the chemical shifts of the α, β, and γ carbons are influenced by the inductive effect of the heteroatom. The nuclear shielding of the α carbon atom decreases, whereas that of the β and γ carbon atoms increases with an increasing electronegativity of the heteroatom. Methyl substituents on the heteroatoms give rise to chemical shift additivity parameters that are similar to magnitude to those found for methylcyclohexane. The γ and δ substituent parameters for the protonation of group VI heteroatoms, for methylation of groups V and VI heteroatoms, and for the formation of halogen adducts of group VI heteroatoms are large and negative. The large upfield chemical shifts are the result of sterically induced charge polarization and sterically induced changes in the geometry of the ring.

10:50 Direct Determination of Aromatic/Aliphatic Carbon Ratio in Solid Fossil Fuels

Gary E. Maciel and *Victor J. Bartuska*

Standard Fourier transform ^{13}C nmr methods are capable of determining the ratio of the number of aromatic carbons to the number of aliphatic carbons, as well as considerably more detailed structural information, on liquid samples. However, because of excessive line broadening of solids, due to dipole-dipole interactions and chemical shift anisotropies, and because of long spin-lattice relaxation times, these standard methods for liquids are not suitable for solids. However, the techniques of dipolar decoupling, especially using the cross polarization approach, and magic-angle spinning show great promise for making it possible to obtain ^{13}C nmr spectra routinely on solid samples. The application of these techniques to solid coal,

kerogen and oil shale samples will be discussed. It will be shown that, using the combination of magic-angle spinning and dipolar decoupling, a direct determination of the ratio of aromatic carbon to aliphatic carbon can be made.

11:10 Proton Enhanced Nuclear Induction Spectroscopy of Fossil Fuels

F. P. Miknis, ERDA, Laramie Energy Research Center, Laramie, Wyoming.

Recent advances have been made in pulsed NMR which allow high resolution ^{13}C NMR spectra to be obtained for solids. The information obtained is similar to that obtained from high resolution NMR spectra of liquids. Some typical proton enhanced ^{13}C spectra of oil shales and coals will be presented. The spectra were obtained at a resonance frequency of 46.6 MHz. In oil shales the spectra consist of a broad band in the aliphatic region, and a broader, weaker band in the aromatic region of the spectrum. Shales from different locations of the Green River Formation show slight differences in the positions of the peak maxima. For coals, the aromatic and aliphatic regions are resolvable such that a direct determination of coal aromaticity can be made.

11:30 Energy Dispersive X-Ray Fluorescence Analysis of Coal, Ores, and Geological Samples

J. A. Cooper, D. B. Schlafke, and D. B. Wheeler, Ortec, Incorporated, Oak Ridge, Tennessee.

Energy dispersive x-ray fluorescence (EDXRF) analysis is a relatively new analytical technique which combines new x-ray detection methods and instruments with the analytical methodology developed over the past 20 or more years for wavelength dispersive x-ray fluorescence (WDXRF) analysis. It is now being used extensively in industry as a routine analytical tool for process control, quality assurance, pollution studies, and many of the materials analysis problems found in the mining industry.

This paper will review the application of EXCRF to the analysis of coal, ores, and other geological material. The analysis of coal for both major and trace elements will be discussed; interelement correction procedures for ores and other geological

materials applied to energy dispersive analysis will be presented; and quantitative results compared. The analytical capabilities of other techniques such as WDXRF, atomic absorption spectrometry, neutron activation analysis, etc., will also be discussed relative to those of EDXRF analysis.

LUNCH –

Session (II)

Chairman: Marvin C. Goldberg, U.S. Department of Interior, Geological Survey, Federal Center, Denver, Colorado.

1:20 Flameless Atomic Absorption Methods for Trace Heavy Metals in Beef Tissues

J. A. Nichols, Analytical Chemistry Facility, Colorado State University, Fort Collins, Colorado.

The method to be described was designed to meet the following requirements: (1) high sensitivity—capability to detect down to 5 or 10 ppb in dry tissue for Pb, Cd, Mo, Ni, As, Se, and Hg; and (2) relative freedom from interferences —determinations should proceed efficiently for all tissue types despite complex matrices.

Representative samples are digested with a catalyzed nitric-perchloric acid digestion, previously described by Cyrus Feldman [Anal. Chem. 46 (1974) pp. 1606-9].

Vapor generation methods may be used directly for As, Se, and Hg.

Chelation is used to preconcentrate Cd, Mo, Ni, and Pb and to eliminate interferences. Ammonium pyrrolidine dithiocarbamate (APDC) forms insoluble chelates; co-precipitation with dichromate and with iron, if present, aids in ensuring large particles in the precipitate. The heavy metal chelates are isolated on a filter pad, which can be redissolved in nitric acid when analyses are scheduled.

Techniques for running molybdenum on the Varian M-63 carbon rod atomizer will be described as an example problem case.

1:40 Atomic Absorption Spectrophotometric Determination of Arsenic and Selenium in Water

D. R. Corbin, Department of Chemistry, and *W. M. Barnard,* Department of Geology, State University of New York College at Fredonia, New York.

An AA spectrophotometric technique, employing parts and modifications of several published methods, is presented as being most practical for the determination of arsenic and selenium in water. A number of parameters have been varied and evaluated to ascertain optimum operational conditions. The non-automated method is relatively inexpensive, uncomplicated, highly sensitive, reproducible, and requires a minimum of skill and manipulation.

Arsenic and selenium are reduced and converted to their hydrides by an aqueous solution of sodium borohydride injected into an acidified sample contained in a reaction vessel by use of a syringe; the hydride is immediately transferred by nitrogen, without collection in a reservoir, to the atomizer of the spectrophotometer and burned in a hydrogen flame. The use of a sodium iodide prereductant added in aqueous form aids in the reduction of arsenate to arsenite to give total inorganic arsenic and permits ready determination separately of inorganic selenite and selenate.

The accuracy of the method was tested by favourable comparison of arsenic and selenium determinations made on Standard Reference Water Samples (U.S.G.S. Water Quality Control Laboratory, Denver) with those made by several laboratories using other methods.

2:00 Optimization of the Hollow Cathode Cell as an Atomization Source for Atomic Absorption Spectroscopy

D. A. McCamey and T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

Workers in atomic absorption spectroscopy have investigated the possible utility of the hollow cathode discharge as an atomization source.[1-5] The hollow cathode is either made of the sample material itself[1] or a portion of the solution to be analyzed is evaporated on the interior of the hollow

cathode.[2,4,5] Certain characteristics of the hollow cathode discharge have attracted these investigations, but have never been fully exploited for practical use. For instance, the discharge operates under a controlled inert atmosphere, which minimizes many interferences commonly observed in flame atomic absorption. Also, the sampling process, rather than a thermal mechanism, is due to sputtering of the sample atoms from the surface of the cathode. For certain sample types, this might prove to be a significant advantage over the thermal atomization systems. The geometry of the electrodes and the resulting discharge characteristics tend to retain the sample in the cavity for relatively long periods. The purpose of this paper is to discuss results of experiments done in this laboratory to further investigate and optimize the use of the hollow cathode discharge cell as an atomization source. The factors investigated are: (1) composition and pressure of the inert filter gas, (2) thermal effects associated with cooling the cathode, (3) supporting cathode material, (4) the geometry of the cell electrodes, and (5) other factors such as ionic buffering, etc. The theoretical implications of an atomic absorption experiment in which the absorbing species is at low pressure will be discussed also.

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[1] Gatehouse, B. M. and A. Walsh, Spectrochim. Acta, 16, 602 (1960).

[2] J. A. Goleb and J. K. Brody, Anal. Chim. Acta, 28, 457 (1963).

[3] J. A. Goleb, Anal, Chem., 35, 1978 (1963).

[4] R. A. Woodriff, G. V. Wheeler, and W. A. Ryder, Appl. Spect., 22, 348 (1968).

[5] B. W. Grandrud and R. K. Skogerboe, Ibid., 25, 243 (1971).

2:20 Digestion of Biological Samples Using Microwave Ovens

F. E. Lichte, E. G. Hinderberger, and S. R. Koirtyohann, Environmental Trace Substances Center, University of Missouri, Columbia, Missouri.

Wet ashing of biological materials is an important step in their analysis for heavy metals. We are presently investigating the use of a microwave oven as a heat source for acid digestions. The major advantages of this heat source over conventional

systems is speed, fewer losses of metals, and more uniform heating.

Details for building the oven, ashing characteristics, and recovery studies will be discussed.

COFFEE BREAK

Session (III)

Chairman: Becky Harrison, Marathon Oil Company, Littleton, Colorado.

2:50 Measurement of Aqueous Suspensions by Fraunhofer Diffraction Spectroscopy

Neil Asting, University of Denver, *M. C. Goldberg* and E. R. Weiner of the U.S. Geological Survey, Lakewood, Colorado.

As a means to measuring the concentration of suspended solids in water, the Fraunhofer diffraction equation was solved. The mathematically obtained intensities were ratioed at various theoretical angles of observation and correlated to the experimental dispersion spectra obtained from laser induced particle scattering. Observations of scattering intensity were made at the extreme forward angles, usually below 12 degrees. It was generally found that monodisperse systems vary by 20 percent from a calculated particle size value and exhibit the expected size distribution in ranges from 0.1 to 0.5 microns. These results are independent of particle density or refractive index.

3:10 X-Ray Diffraction of Rare Earth Oxides

R. Botdorf, Pennsylvania State University-Berks Campus, Reading, Pennsylvania, and Gregory McCarthy, Pennsylvania State University, University Park, Pennsylvania.

X-ray diffraction methods have been utilized to determine crystal data for some rare earth oxides of iron and gallium. The specimens were prepared from oxides of dysprosium, erbium, thulium, and ytterbium together with iron and gallium.

A least squares computer program was used to refine the x-ray powder data. Calculated interplanar spacings agree closely with observed values. Relative peak intensities have been calculated from intensities of reflections emitted from the various atomic planes. In addition, one reference intensity

measurement was made with corundum for each sample. Cell parameters and other data will be discussed.

The general formula of these rare earth oxides is such that three moles of trivalent rare earth atoms and five moles of either trivalent iron or gallium atoms are equivalent with respect to charge to three moles of divalent metal, two moles of a trivalent metal, and three moles of tetravalent silicon as found in the formula for minerals with the same structure.

3:30 Energy Transfer Process in the (Y, Yb, ER)F_3 System during Infrared-to-Visible Conversion

D. E. Ettinger and T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

The process of upconversion has been studied in the $(Y_{.80}Yb_{.19}Er_{.01})F_3$ system. Visible emission at 660 nm, 550 nm, 520 nm, 409 nm and 379 nm has been detected on excitation with 970 nm radiation. The 660 nm, 409 nm and 379 nm bands have been found to result from 3-photon absorption processes at 195 °K. The 550 nm and 520 nm bands result from a 2-photon process at this same temperature and low incident IR intensity. Back-transfer of energy ($Er^{3+} \rightarrow Yb^{3+}$) has been shown to play a role in the excitation of the 660 nm band as well as in the excitation of the 550 nm and 520 nm bands when the incident IR intensity is high. These and other features of upconversion in the (Y, Yb, Er)F_3 system will be discussed.

Tuesday, August 3, 1976

Session (IV)

Chairman: Steve Valente, Custom Chemicals Company, Denver, Colorado.

8:30 Industrial Applications of ICP Spectroscopy

A. J. Ellgren, R. J. Lewandowski, R. G. Pankhurst, Union Carbide Corporation, Central Scientific Laboratory, Tarrytown, New York.

The application of a multi-channel Direct Reading Spectrometer with an Inductively Coupled Plasma source to industrial analytical projects and problems is described. Preliminary tests of

Inductively Coupled Plasma (ICP) spectrometry in regard to the following proposed capabilities have been performed: (1) "true" multi-element capability, (2) ease of standardization, (3) precision and accuracy under standard conditions, (4) dynamic range (magnitude of linear response), (5) lack of "matrix effects", and (6) cost effectiveness.

The preliminary tests have been conducted on up to thirty-eight different elements in the following matrices: (1) Water, (2) Alumina (solubilized), and (3) Aluminum alkoxide solutions.

Data is presented for most common metals and some not so common elements (e.g., Ga, Pd, Rh, La, Ce, and Pt) in the above-mentioned matrices.

The information presented represents only preliminary tests on projects and current method development which will continue throughout the year.

Projected applications of ICP spectroscopy will also be briefly discussed as relevant to the analtyical requests in a consolidated R & D center.

8:50 Applications of Multiple-Wavelength Detection to Atomic Spectroscopy

F. S. Chuang, D. F. S. Natusch, and K. R. O'Keefe, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

The utility of background correction at several analytical wavelengths in multielement atomic spectroscopy has been investigated. Conventional multiple wavelength detection and the use of a solid state diode array will be discussed with respect to this application and results will be presented.

9:10 Dynamic Background Correction of D.C. Arc Spectrometry

G. W. Johnson and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

The advantages of using dynamic background correction at each analytical wavelength have been determined for D.C. arc excitation. Results which demonstrate these will be presented and the reasons for the improvements observed will be discussed.

9:30 Effects of Hydrogen on Excitation in a D.C. Plasma

I. T. Urasa and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

The addition of small amounts of hydrogen to a D.C. plasma in argon causes significant enhancements in the excitation properties of the system. The changes observed and the apparent causes will be described and the mechanistic aspects will be discussed.

COFFEE BREAK –

Session (V)

Chairman: Harold Todd, Gates Rubber Company, Denver, Colorado.

10:20 Characterization of Treated Glass Surfaces by Combined Ion Scattering Spectrometry and Secondary Ion Mass Spectrometry

H. E. Mishmash, 3M Company, Central Research Labs, St. Paul, Minnesota.

With the new techniques now available for the analysis of the outermost monolayers of a surface, the analyst has the opportunity to study some of the interesting phenomonon that were previously accepted but perhaps unexplained or proven. One material which falls into this category probably more than any other is glass. This report deals with the changes that occur when glass is subjected to such common surface treatments as cleaning, polishing or etching.

The instrumentation used was a combined ion scattering spectrometer (ISS) and a secondary ion mass spectrometer (SIMS). In ISS, a surface is bombarded with a beam of noble gas ions and then the energies of the scattered ions are analyzed. These energies are related to the mass of the surface atoms permitting chemical analysis. During this ion bombardment, atoms are also sputtered from the surface and these are monitored with the quadropole of the SIMS. The sputtering, or milling away of the surface, also gives the method the capability of depth profile analysis, which is necessary for this type of study.

A variety of surface treatments were studied and include among others such procedures as HF vapor etch, HF liquid etch, chromic acid cleaning, and polishing or rubbing with different materials. The changes that result, along with the degree or depth of the change, can be useful in determination of the mechanism for some of the observed ion migrations. In addition, knowledge of the true surface after a treatment can be invaluable for use of that surface for other applications and in the explanation of observed phenomonon whose cause has previously only been speculated.

10:40 Electron Impact-Photon Induced Ionization of CO_2

J. H. Weber, ERDA, Laramie Energy Research Center, and A. B. Denison, J. M. Phillips, J. M. Knox, Department of Physics and Astronomy, University Wyoming, Laramie, Wyoming.

We have developed a technique using simultaneously an electron beam and optical radiation in the ionization region of a mass spectrometer. This allows one to obtain information concerning molecular excited states. By varying the electron impact energy and the optical wavelength we have been able to study a variety of excited state effects including photo-ionization from excited states. One molecule which exhibits such an effect is CO_2. Since our original paper on the optically modified spectrum of CO_2 we have obtained new experimental data and have improved the theoretical description of the mechanism involved in this photo-assisted ionization phenomenon.

A mechanism is proposed by which the most loosely bound electron in the CO_2 system is excited into a high Rydberg level leaving an "ionic core" which then may be photon excited to a level near the first ionic excited state. This combined double excitation leaves the system with too much energy to be stable and one electron is ejected. This latter process is essentially auto-ionization and the cross section may in principle be calculated.

11:00 Measurement of Kinetic Energy of Ion Fragments in a Mass Spectrometer

A. I. Ossinger, Environmental Protection Agency, Denver, Colorado, and *E. R. Weiner,* Department of Chemistry, University of Denver, Denver, Colorado.

A complete accounting of the energy involved in molecular dissociation must include the kinetic energy of the dissociating fragments. Various mass spectrometric techniques have been developed to measure the kinetic energy of charged fragments from dissociating ions.[1] The data is being used to help compute bond energies, ionization potentials and heats of formation of ionic species. The information also is useful for testing and refining the statistical theory of unimolecular decomposition. A new method for measuring the kinetic energies of ionic fragments from electron impact in a time-of-flight mass spectrometer is described. The method measures the angular spread of the ion beam which originates from a point source and is accelerated in a uniform electric field. Experimental results are given for ion fragments from propane, 1-butene, methyl chloride, methyl bromide, ethyl chloride, ethyl bromide, vinyl chloride and vinyl bromide. The new method permitted the first reported observation of dissociation processes leading to two discrete excess kinetic energies for a given ion fragment. Previously, only one value of excess kinetic energy has been reported for any given fragment. Where they can be compared, the other measured values of kinetic energy agree well with measurements by different methods.

[1] A. L. Burlingame, R. E. Cox, and P. J. Derrick, 46, 248R (1974).

11:20 Determination of Permeation Rates by Dynamic Mass Spectrometry

T. L. McFeeters, Rockwell International, Golden, Colorado.

Permeation rates of hydrogen, oxygen, nitrogen and carbon dioxide through such materials as neoprene, Hypalon, Viton, and sheet materials formed from multiple layers of such materials have been determined.

The use of a Bendix MA-3 time-of-flight mass spectrometer, dynamic mass spectrometry techniques, and a special sample manifold for the determination of permeation rates is discussed.

Computer processing of data, with a history file of results featuring result retrieval by permeant, sample material, or by specific sample identification is briefly discussed.

Examples of results obtained are presented along with statistical data on each permeation rate determined.

LUNCH –

Session (VI)

Chairman: Roland Manning, Ball Brothers Research Corporation, Boulder, Colorado.

1:10 Measurements of Stratospheric Halocarbon Distributions Using Infrared Techniques

D. G. Murcray, A. Goldman, F. S. Bonomo, W. J. Williams, J. J. Kosters, University of Denver, Denver, Colorado.

Absorption bands of CF_2Cl_2, $CFCl_3$, and CCl_4 have been observed in infrared sunset solar spectra in the 800-1000 cm^{-1} region from 30 kilometer altitude during a balloon flight made in September 1975. Infrared absorption bands were used to derive the distribution of these constituents in the upper troposphere and lower stratosphere. The results are compared with 1968 data and with current results of other research groups. Distributions were obtained from quantitative laboratory absorption measurements of strong bands of the pure compounds, carried out at 25 °C in absorption cells of various lengths to obtain curves of growth. Statistical-band-model analysis resulted in band metal parameters and an integrated intensity which provided a basis for measurement of the atmospheric distributions of these halocarbons.

More recent work with a ground-based Fourier Transform Infrared Spectrometer has demonstrated the feasibility for monitoring these halocarbons plus HNO_3 from the ground.

1:30 Vibrational and Conformational Analysis of Some Alkyl Bromides

G. A. Crowder and M. Jalilian, Department of Chemistry, West Texas State University, Canyon, Texas.

Infrared and Raman spectra were obtained for the series of n-alkyl bromides n-C_3H_7Br through n-$C_6H_{13}Br$. Simultaneous normal coordinate calculations were made for the two conformations of each compound that have all carbons coplanar, with 21 force constants of a 48-parameter modified valence force field being refined to provide the best fit between observed and calculated frequencies. The average difference between observed and calculated wavenumbers for 186 frequencies of the eight conformers below 1500 cm^{-1} was 5.8 cm^{-1}, or 0.6%. The force constants obtained in this way were used to make zero-order calculations for n-$C_7H_{15}Br$, with the average difference between observed and calculated wavenumbers for 78 values below 1500 cm^{-1} being 6.1 cm^{-1}. Vibrational spectra were also obtained for several branched-chain primary alkyl bromides, and the spectra were interpreted with the aid of normal coordinate calculations.

This work was supported by The Robert A. Welch Foundation, Houston, Texas.

1:50 The Electronic States and Photochemistry of Diiodomethane

F. Stein, Chemistry Department, Western State College, and S. Strickler, Department of Chemistry, University of Colorado, Boulder, Colorado.

In a solution of diiodomethane, CH_2I_2, three electronic bands are observed at 34,000, 40,000 and 47,000 cm^{-1}. A study was proposed to characterize the photochemistry of CH_2I_2 and the electronic states of the photoproducts at 34,000 cm^{-1}.

A broad band was produced around 34,000 cm^{-1} by using a high-pressure mercury 1 amp (G.E. AH6) with a pyrex filter. The experiment at 40,000 cm^{-1} was carried out with a 2537A reactor.

The CH_2I_2 was irradicated in the presence (separately) of cis- and trans-2-pentene. The CH_2 molecule was produced and reacted with the alkanes to give cyclopropanes. According to P. S. Skell, singlet CH_2 undergoes stereospecific addition and triplet CH_2 undergoes non-stereospecific addition to the carbon-carbon double bond. It was found that the reaction was stereospecific.

Our results indicated that radiation at both 34,000 and 40,000 cm^{-1} results in the production of a molecular I_2 and CH_2 species and that the CH_2 is produced in the singlet state rather than in its triplet ground state.

2:10 Gas Phase EPR Spectroscopy of Electronically Excited Species

W. E. McDermott, Department of Chemical and Biological Sciences, United States Air Force Academy, Colorado.

Electron Paramagnetic Resonance Spectroscopy is used to determine the concentrations of ground state and electronically excited molecular oxygen in the flowing afterglow of a microwave discharge. A comparison with photometric measurements is made. Upon titration with molecular iodine downstream of the discharge, iodine atoms are produced which also are measured via EPR spectroscopy. The kinetics of this process is discussed with reference to this system as a possible iodine atom laser pumping mechanism.

COFFEE BREAK —

Session (VII)

2:40 Fluorescence Interferences in Raman Scattering from Combustion Products

D. P. Aeschliman, Sandia Laboratories, Albuquerque, New Mexico, and R. E. Setchell, Sandia Laboratories, Livermore, California.

Broad-band laser-induced fluorescence has been observed in Raman scattering from the exhaust

of an internal combustion engine. This work was performed to identify potential spectral interferences to general studies of combustion processes using Raman spectroscopy. In previous work[1] exhaust gases from an engine operating on gasoline were passed through an optical cell within the cavity of an argon-ion laser, and Raman spectra and fluorescence backgrounds were observed using a single ¾m. monochromator. Various exhaust conditioning devices were used to eliminate water and aerosols, and the results suggested that the primary source of the fluorescence was aerosols of hydrocarbons or other organic compounds. This was in contrast to the observations of Roquemore and Hodgson[2] who concluded that fluorescence in gas turbine exhaust excited by a nitrogen laser at 3371 Å were due to gas-phase hydrocarbons.

The present study examined the fluorescence induced by an argon-ion laser at 4880 A, occurring in the exhaust of an internal combustion engine operating on different fuels and fuel/air mixtures. A broad-band fluorescence was observed in all cases, with the highest and lowest intensities observed when operating on rich propane, and lean methane, respectively. Elimination of the fluorescence background by various exhaust conditioning devices confirmed the previous conclusion that hydrocarbon aerosols are the principal fluorescence source. In a separate series of experiments, Raman studies using an argon laser and both single and double monochromators were performed on the liquid condensed from the exhaust gases in a refrigerated cold-trap. In addition to the anticipated Raman bands of water, the liquid samples showed a broad-band fluorescence quite similar to that observed in the exhaust gases. Conventional analysis of the liquid samples are in progress to identify possible fluorescent species.

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[1] D. P. Aeschilman and R. E. Setchell, App. Spectros., 29, 426 (1975).

[2] W. M. Roquemore and F. N. Hodgson, Vol 2, Paper 27-4, Int. Conf. on Environmental Sensing and Assessment, Las Vegas, Nevada (Sept. 14-19, 1975).

3:00 Raman Spectroscopy Measurements Within an Internal Combustion Engine

R. E. Setchell, Sandia Laboratories, Combustion Research Division, Livermore, California.

A challenging area of combustion research is the development of new diagnostic techniques for measuring temperature and species concentrations within steady and unsteady combustion systems. Raman spectroscopy has been shown to be capable of such measurements in relatively simple laboratory flames,[1-4] but applications to practical combustion devices remain to be domonstrated. Difficulties that can be anticipated include low sensitivity, broad-band spectral interferences from emission and laser-induced fluorescence,[5] errors introduced by turbulence fluctuations in local gas conditions,[4] and the unknown Raman scattering properties of many flame species at elevated temperatures.

An experimental facility has been assembled to investigate the feasibility of Raman spectroscopy measurements in internal combustion engines. A single-cylinder L-head engine has been modified with sapphire windows to permit both the horizontal passage of a focused laser beam through the combustion chamber and the vertical collection of light scattered at a right angle to the beam. The collected light is passed through a ¾-meter single spectrometer and detected with a PAR Model 1205D Optical Multichannel Analyzer (OMA). The OMA is operated in a gated mode using a timing circuit driven by a crankshaft encoder. The width of the OMA gating pulses can be adjusted from 100-1000 μsec and the spectrometer/OMA combination currently provides a simultaneous spectral view of 12 nm resolved into 500 channels.

The present experimental configuration incorporates a CW argon-ion laser producing up to 12 watts at 488 nm in a two-pass scattering mode. Results will be presented for the initial phase of the investigation in which spectral interferences from emission and laser-induced fluorescence are examined, and the sensitivity of the Raman system for pre-ignition measurements of local fuel/air ratios is determined. A subsequent phase of the

investigation will incorporate a pulsed dye laser for Raman scattering from the post-flame gases.

[1]M. Lapp, "Flame Temperatures from Vibrational Raman Scattering," in Laser Raman Gas Diagnostics, M. Lapp and C. M. Penney, Eds., Plenum Press, New York, 1974, p. 107.

[2]R. E. Setchell, "Analysis of Flame Emissions by Laser Ramon Spectroscopy," Western States Section/The Combustion Institute, Paper 74-6, 1974.

[3]A.C. Eckbreth, "Laser Raman Gas Thermometry," AIAA Paper 74-1144, 1974.

[4]R. E. Setchell, "Time-Averaged Measurements in Turbulent Flames Using Raman Spectroscopy," AIAA Paper 76-28, 1976. Accepted for Progress in Astronautics and Aeronautics, 1976.

[5]D. P. Aeschliman and R. E. Setchell, "Fluorescence Limitations to Combustion Studies Using Raman Spectroscopy," Appl. Spectrosc. 29, 1975, p. 426.

3:30 A New Computerized Solid-State Array Spectrometer for the Detection of Liquid Chromatography Effluents

R. E. Dessy, ***W. D. Reynolds,*** W. G. Nunn, C. A. Titus, National Center for Toxicological Research, Department of Health, Education and Welfare, Jefferson, Arkansas.

A third generation multi-wavelength array spectrometer was developed as a detector for the high resolution liquid chromatographic characterization of metabolites. The design features include a PDP-8/e mini-computer, matched pair of linear photodiode (256 element) arrays (Reticon), holographically ruled gratings, fiber optics, flow cells and high intensity Xenon light source. The wavelength range is 256 nM differential with 1 nM resolution and can be independently adjusted in the spectral range of 200 to 800 nM. Correction for the quantum efficiency curve is made on both of the cooled (−30 °C) photodiode arrays by an assembly language sub-routine. The system is capable of 20 spectra/second (250-506 nM) in a dual-beam mode. The dynamic range and linearity of the photodiode arrays is approximately 4000:1. Special features include mini-computer driven signal enhancement via integration as a function of signal strength. The display output includes presentation of the total absorption chromatogram (TAC) vs. elution time in both real and post-run time as well as selectable signle absorption band

(ABC) (e.g., 280 nM) vs. elution time (post-run time). Application of this dedicated mini-computer automated LC/UV system for the separation and characterization of the metabolites of a carcinogen, 4-ethylsulfonyl-1-napthalenesulfonamide (ENS), will be discussed.

3:50 The Use of Alpha Spectrometry in Radioanalysis

T. F. Rees, Rockwell International, Golden, Colorado.

Alpha Spectrometry is the most useful analytical tool for identifying and quantifying alpha emitting radionuclides. Alpha particles are emitted from the nucleus with characteristic energies that can be determined using charge sensitive detectors and a pulse height analyzer. Specific radio-isotopes are determined by chemical separation from the sample matrix and by analyzing the alpha energies. An introduction to alpha spectrometry using the analysis of plutonium in soil to illustrate the technique is given.

POSTER SESSIONS

Monday 1:30 to 3:30 p.m.
(Authors present 2:00 to 2:30 p.m.)

Permeation Tubes for Dynamic Mass Spectrometry Calibration

T. L. McFeeters, Rockwell International, Golden, Colorado.

Quantitative dynamic mass spectrometry requires calibration of the mass spectrometer in terms of a components flow rate through the ion source (moles/sec/millimeter recorded peak height, etc.).

Very few compounds are commercially available in the form of standards, the notable exception being helium, with commercially available known helium leaks commonly in use for leak detector calibration.

This paper presents a brief discussion of dynamic mass spectrometry and describes the construction, calibration and use of vacuum service permeation tubes in dynamic mass spectrometry.

Photochemistry of Halocarbons

F. Stein, Chemistry Department, Western State College, Gunnison, Colorado.

A general discussion of the photochemistry of molecules will be presented.

Tuesday 8:30 to 11:30 a.m.
(Authors present 9:30 to 10:00 a.m.)

Applications of a GC/MS Data System at Rocky Flats

J. R. Turbett, K. J. Grossaint, and D. I. Hunter, Rockwell International, Golden, Colorado.

Applications of an automated gas chromatograph –mass spectrometer data system will be presented. The GC/MS system is used as a tool for analtyical problem solving and trace organic identification in the industrial laboratory.

Examples of identification of organic components in complex mixtures will be discussed. A discussion of the hardware will also be included.

Identification of Gunshot Residues by Flameless Atomic Absorption Spectrometry

Dr. Richard B. Lehmann, Colorado Bureau of Investigation, Denver, Colorado.

The technique of collecting gunshot residue swabs is a commonly used method of determining whether a subject has recently fired a hand gun. Flameless atomic absorption is utilized by determining the levels of barium and antimony residue. The sensitivity, limitations, and the usefulness of this procedure will be discussed.

Tuesday 1:30 to 3:30 p.m.
(Authors present 2:00 to 2:30 p.m.)

Automated Data Processing for Mass Spectrometers

Don Hagge, INCOS, Incorporated, Berkeley, California.

Examples of acquisition of spectral data from several types of scanning mass spectrometers will be presented. Computer control allows the operator to obtain displays of output of the system performance, and to tailor scan and acquisition parameters for optimum performance. GC/MS

data obtained by the INCOS 2300 Mass Spectrometer data system can be manipulated to provide the chemist with visual displays of Reconstructed Gas Chromatograms, chromatograms based on individual fragment ions (Mass Chromatograms), and three dimensional plots including the a.m.u. of fragment ions, their intensity, and time or scan number.

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